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Bituminous Roof Sealing Membranes as Major Sources of the Herbicide (*R*,*S*)-Mecoprop in Roof Runoff Waters: Potential Contamination of Groundwater and Surface Waters

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During a field study on the occurrence and behavior of pesticides during artificial infiltration of roof runoff, the herbicide *R*-mecoprop and its *S*-enantiomer were detected in roof runoff in much higher concentrations (up to 500 μg/L) than in the corresponding rainwater. We hypothesized in the foregoing paper in this issue that the root protection agent Preventol B 2 in the bituminous sheets, which is a bi-ester of (*R*,*S*)-mecoprop (see Figure 1), was the source of these compounds. In this work, the occurrence and variations of (*R*,*S*)-mecoprop in the runoff from different flat roofs were investigated. It is shown that concentrations of a few micrograms per liter at an R to S enantiomeric ratio (ER) of 0.8−1.4 can permanently be expected in roof runoff from flat roofs which have Preventol B 2 containing sealing membranes incorporated. The major factors that govern the release of (*R*,*S*)-mecoprop are the type of bituminous sheet, the biological activity, and the intensity of the applied rooftop greening. A field study in the Greifensee catchment area revealed that wastewater treatment plants (WWTPs) are a major source of (*R*,*S*)-mecoprop which most probably originates from construction materials equipped with Preventol B 2. A comparison of the (*R*,*S*)-mecoprop loads from flat roofs and from agricultural applications into surface waters revealed that these loads were in the same order of magnitude.

Introduction

In the course of a field investigation on the occurrence and the behavior of pesticides during artificial infiltration of roof runoff (for details, see companion paper (*1*)), the herbicide *R*-mecoprop (Figure 1) as well as its herbicidal inactive enantiomer *S*-mecoprop were detected in concentrations up to a few hundred micrograms per liter, exceeding the Swiss and European Union drinking water standards of 100 ng/L by up to a factor of 10^4. Since these concentrations were several orders of magnitude higher than the measured concentrations of the two compounds in rainwater, a source other than the atmosphere had to be present. The most likely candidate for the source of (*R*,*S*)-mecoprop was found to be a sealing polymer-modified bituminous roofing membrane present on two of the flat gravel roofs. This membrane contained the roof protection agent Preventol B 2 (about 1 wt %) which, when hydrolyzing, releases (*R*,*S*)-mecoprop (see Figure 1).

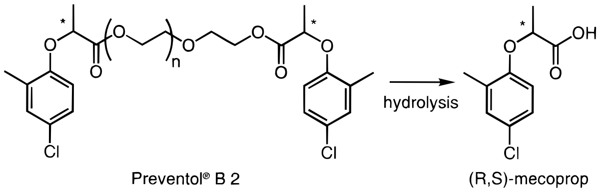

FIGURE 1. Structures of Preventol B 2 (M-PEG-M), and (*R*,*S*)-mecoprop (M). Stars indicate chiral centers. Note that Preventol B 2 is a technical product with a poly(ethylene glycol) (PEG) chain of variable length.

The application of Preventol B 2 comprises bituminous construction materials such as roofing felts, sealants, insulations, and asphalt mixtures, but also the protection of rubber seals against root penetration (*2*). In Switzerland, the annual use of Preventol B 2 in bituminous sealing membranes is about 30 t (*3*), which is in the same order of magnitude as the total amount of *R*-mecoprop applied in agriculture. Because Preventol B 2 has already been used for at least 10 years, it can be assumed that several hundred metric tons are presently incorporated in rooftop sealings in Switzerland. When it is considered that roof runoff becomes increasingly important for recharging groundwater used as drinking water resource, knowledge about the processes that control the input of (*R*,*S*)-mecoprop from roof sealing, and possibly of other chemicals used for similar purposes, is essential. Furthermore, quantitative data on the total amount of such biocides introduced into the environment by roof runoff are required for a proper risk assessment.

In this paper, we summarize the results of a series of laboratory and field experiments conducted (i) to confirm the hypothesis that roof sealings are major sources for (*R*,*S*)-mecoprop in roof runoff, (ii) to identify the processes that determine the release of (*R*,*S*)-mecoprop from the roofs, and (iii) to generate quantitative field data for assessing the potential impact of roof-derived (*R*,*S*)-mecoprop on the quality of natural waters, particularly of groundwater and artificial stormwater infiltration sites. To this end, artificial rain events on different model roofs and laboratory experiments were conducted to investigate the factors controlling the release of (*R*,*S*)-mecoprop. Furthermore, a number of field studies under natural conditions were conducted to gather data for estimating annual (*R*,*S*)-mecoprop fluxes from roofs. Moreover, measurements of (*R*,*S*)-mecoprop in WWTPs and tributaries in the catchment area of lake Greifensee were used to elucidate the importance of Preventol B 2 containing sealing membranes as a nonagricultural source of this compound for surface waters. The results of this study demonstrate that compounds exhibiting biocidal properties and/or precursors of such compounds present in construction materials may represent a major source for the occurrence of such compounds in natural waters.

Experimental Section

Materials. Polymer-modified bituminous roofing membranes (type EP4 WF, SIA-281) were a donation from the three main producers in Switzerland, namely Soprema (Spreitenbach, Switzerland), Paul Bauder AG (Arlesheim, Switzerland), and Vaparoid AG (Dulliken, Switzerland), subsequently named products 1, 2, and 3, respectively.

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Preventol B 2 is a product from Bayer Material Protection (Leverkusen, Germany) and was received from agevogel (Zürich, Switzerland). (*R*,*S*)-mecoprop and 2,4,5-T were purchased from Riedl-de Haën (Seelze, Germany). $Ca(NO_3)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, H_2SO_4, KOH, NaN_3, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $(NH_4)_2SO_4$, and $MnSO_4 \cdot H_2O$ were purchased from Merck (Darmstadt, Germany), and H_3BO_3, KH_2PO_4, $MgSO_4 \cdot 7H_2O$, $NaHCO_3$, Na_2CO_3, $Na_2HPO_4 \cdot 2H_2O$, $NiSO_4 \cdot 7H_2O$, and $ZnSO_4 \cdot 7H_2O$ were from Fluka AG (Buchs, Switzerland). Deionized water was further purified with a Nanopure water purification device (NANOpure 4, Skan, Basle, Switzerland).

Mineral Medium Solution and Inoculation Solution for Hydrolysis and Elution Experiments. The mineral medium used for nonsterile laboratory experiments consisted of a phosphate buffer ($KH_2PO_4-Na_2PO_4$, pH 7, 0.01 M for hydrolysis, and 0.1 M for elution experiments) containing 0.12 g/L $(NH_4)_2SO_4$, 73 mg/L $MgSO_4 \cdot 7H_2O$, and 1 mg/L $Ca(NO_3)_2 \cdot 4H_2O$. The following trace elements were added at 0.2 mL/L from an acidified (H_3BO_3, 0.1 g/L; H_2SO_4, 5 mL/L) stock solution containing 2.5 g/L $FeSO_4 \cdot 7H_2O$, 0.75 g/L $MnSO_4 \cdot H_2O$, 1.3 g/L $ZnSO_4 \cdot 7H_2O$, 0.25 g/L $CuSO_4 \cdot 5H_2O$, 0.3 g/L $Co(NO_3)_2 \cdot 6H_2O$, 0.12 g/L $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and 0.1 g/L $NiSO_4 \cdot 7H_2O$.

The inoculum was prepared from soil material sampled from the flat gravel roof with humic layer in Grüze (Winterthur, Canton Zürich, ref *1*) that was equipped with Preventol B 2 containing polymer-modified bituminous roofing membranes. Note that this material was in immediate contact with the bituminous layers. A few hundred grams of the soil material was suspended in the mineral medium for 3 h. After 1 h of sedimentation, the supernatant was passed through an 8 μm filter (cellulose nitrate filter, diameter 5 cm, Satorius, Goettingen, Germany) and the filtrate was used as an inoculum.

Laboratory Experiments. Hydrolysis. A standard solution of Preventol B 2 in methanol was prepared by adding 1 g of the Preventol B 2 to 100 mL of methanol. Five liters of each a 0.01 M K/Na_2 phosphate buffer (pH 7), a 0.01 M K/Na_2 phosphate buffer (pH 7) with the mineral medium and 50 mL of the inoculum, a 0.01 M H_3BO_3 buffer (0.005 M KOH added to yield pH 9), and a 0.01 M carbonate buffer (pH 10), respectively, were then spiked with 50 μL of the 0.1 g/L standard solution. The resulting Preventol B 2 concentration was 100 μg/L, corresponding to 73 μg/L of the "bound" (*R*,*S*)-mecoprop (assuming a tetraethylene glycol chain). All buffers except the one containing the inoculum were autoclaved prior to the addition of Preventol B 2, which caused a volume reduction of around 10% (considered in calculations). These solutions were stored at 25 °C. Due to different ethoxylene chain lengths in the technical product it was impossible to quantify Preventol B 2; however, the hydrolysis products *R*- and *S*-mecoprop were determined in each of the samples at different times in duplicate for the sterile setup at pH 7, and in triplicate for all other setups. Sample volumes of 500−1000 mL were used for determination of the initial (*R*,*S*)-mecoprop concentration, and 100 mL was used for the later measurements. Before analysis, the hydrolysis of Preventol B 2 in samples from experiments at pH 9 and 10 was slowed down by decreasing the pH to 7 with the addition of 5 mL of a 1 M phosphate buffer (pH 7).

Elution Experiments. Circular pieces with a diameter of 4.0 cm were punched out of the polymer-modified bituminous roofing membranes from the three producers, and each was put into the lid of a 100 mL Duran-Schott flask, resulting in an exposable surface area of 7 cm^2. The flasks were filled with 100 mL of the probe solution, the lids were tightly screwed onto the flasks, and the samples were shaken on a horizontal shaker at 150 min^{-1}. A 0.1 M phosphate buffer (pH 7), a 0.1 M phosphate buffer (pH 7) containing mineral medium and 1 mL of the inoculum as well as a 0.1 M carbonate buffer (pH 10) served as probe solutions. The phosphate buffer without inoculum, and the carbonate buffer were autoclaved prior to usage. Product 1 membranes were exposed to the sterile phosphate and carbonate buffers and kept at 4 and 25 °C, respectively. Exposition of product 1 to the nonsterile phosphate buffer was performed at 25 °C only. Product 2 and 3 sheets were only exposed to sterile pH 7 solutions at 25 °C. Sterile conditions were assured by addition of 0.6 g/L NaN_3 (N_3 did not influence the experiments) to all samples, except one (product 1, pH 7, 25 °C, with inoculum). (*R*,*S*)-Mecoprop concentrations in the 100 mL buffer solutions were measured in duplicate (product 1 at 4 °C, and products 2 and 3) or in triplicate (all other samples) for each sample setup at 4−5 different times. Sample volumes ranged from 10 (diluted to 100 mL with Nanopure water) to 50 mL. To assess a possible direct elution of Preventol B 2 (or the intermediate hydrolysis product, i.e., the monoester with an alcohol moiety, M-PEG, see Figure 1), half of the sample volumes from product 1 samples exposed to pH 7 at 25 °C were adjusted to a pH of 10 by adding 250 mL of 10 M KOH and set aside for at least 2 h. This allowed the fast base-catalyzed hydrolysis of Preventol B 2 in solution, and then the subsequent analysis of the reaction product.

Field Sites, Sampling, and Sample Preparation. For the investigation of the leaching of (*R*,*S*)-mecoprop from flat roofs, model green flat roofs with an area of 25 m^2 each were used. Both roofs were part of a model roof system set up by the Ingenieurschule Burgdorf (Canton Bern, for details, see ref *4*). The first one (roof A) was designed by Paul Bauder AG (Arlesheim, Switzerland), with a root resistant Plant E bitumin membrane from the constructor and an intensive rooftop greening. The second one (roof B) was constructed by Optima-Werke (Münchenstein, Switzerland), using a root resistant Sopralen EV3 bitumin sheet from Soprema (Spreitenbach, Switzerland) and had only a marginal rooftop greening. Appearance in roof runoff and elution dynamics of (*R*,*S*)-mecoprop from these roofs were investigated by exposing them to artificial rain events: 18 L/m^2 of tap water ((*R*,*S*)-mecoprop concentration <30ng/L) was uniformly sprayed with a constant flow onto each of the model roofs within 30 min. Sampling of sequential roof runoff was performed manually.

The two flat roofs in Grüze were equipped with polymer-modified bituminous roofing membranes from Soprema (Spreitenbach, Switzerland), containing Preventol B 2 (EP4 WF). This field site and the sampling procedure are described in detail in ref *1*.

To evaluate the importance of bituminous sheets as sources of (*R*,*S*)-mecoprop in surface waters, water samples from Lake Greifensee, which is located 10 km east of Zurich (for details, see ref *5*), and samples from its major tributaries Aa and Aabach and from effluents of the WWTPS in the catchment area were taken and analyzed. All samples were stored at 4 °C in the dark and analyzed the next day. Prior to analysis, samples were allowed to reach room temperature and then filtered (cellulose nitrate filter, diameter 5 cm, pore size 0.45 μm; Satorius, Goettingen, Germany).

Analysis. *R*- and *S*-mecoprop were determined by the previously described multiresidue pesticide analytical method (*6*). To account for the drastically higher concentrations, a second internal standard, namely 2,4,5-T (10 μg) was added to all samples, and the sample volume was adjusted to the expected concentration range (50−1000 mL). Separation of *R*- and *S*-mecoprop was performed with a homemade fused silica capillary column (OV-1701-OH + 25% 6-tertbutyl-2,3-dimethyl-β-CD, 0.13 μm film thickness, 0.25 mm i.d., 15 m). The oven temperature was programmed as follows: 1 min at 60 °C, to 120 °C at 20 °C/min, to 150 °C at 4 °C/min, to

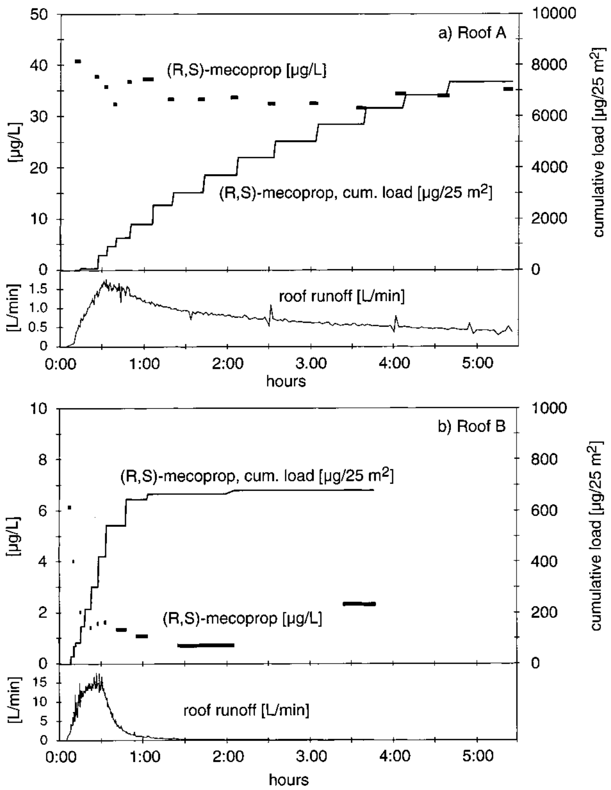

FIGURE 2. **(*R,S*)-Mecoprop in model roof A (a) and model roof B (b) runoff. For each roof, the (*R,S*)-mecoprop concentrations and cumulative loads (upper box), and the respective roof runoff (lower box) are shown. (*R,S*)-Mecoprop concentration in the artificial rainwater was <30 ng/L, and the ERs of roof A and roof B were 0.97 ± 0.02 ($n = 15$) and 0.94 ± 0.24 ($n = 12$), respectively.**

230 °C at 20 °C/min, and 5 min at 230 °C. Linearity of the analytical method (i.e., SPE, and separation and detection with GC/MS) was confirmed up to 30 μg (*R,S*)-mecoprop, irrespective of the sample volume. When using 2,4,5-T for quantification, relative recovery in roof runoff samples was 80%, method precision 14%, and the method detection limit 40 ng/L. Relative recoveries of (*R,S*)-mecoprop from 0.1 M buffers were similar at pH 7 and 10 (data not shown).

Results and Discussion

Model Experiments. Figure 2 shows the time courses of the (*R,S*)-mecoprop concentrations and loads in the runoff from the two model flat roofs during an artificial rain event. As is evident, from both roofs, significant amounts of (*R,S*)-mecoprop were leached; however, the two roofs exhibited very different runoff dynamics. About 1 order of magnitude higher (*R,S*)-mecoprop concentrations and loads were found in the runoff from the roof with the more intensive rooftop greening (roof A), which is the major reason for the longer residence time of the water on this roof (compare bottom parts of Figure 2, parts a and b). However, the observed different (*R,S*)-mecoprop elution behavior from the two roofs cannot only be attributed to the different water residence times; other factors including the bituminous sealing membranes used, the microbial activites at the membrane surfaces (see enantiomeric ratios given in Figure 2 captions), and the root intensities and their penetration into the membranes have to be considered. In a series of some preliminary laboratory experiments, some of these factors were investigated.

Figure 3 shows that, at pH 7, the abiotic hydrolysis of Preventol B 2 is primarily base-catalyzed ($k_B = 5.5 \pm 0.7 \times 10^3$ M^{-1} s^{-1}), and that, at pH 7 and 25 °C, the presence of microorganisms decreased the hydrolysis half-life by more than an order of magnitude. The finding that equal amounts of *R*- and *S*-mecoprop (enantiomeric ratio (ER): 1.00 ± 0.03 ($n = 71$)) were formed by the abiotic hydrolysis under the various conditions investigated is in agreement with the fact that racemic (*R,S*)-mecoprop is used for the production of Preventol B 2. A similar result was obtained for the microbially catalyzed hydrolysis; however, with increasing time, due to further degradation of the two enantiomers, the ER increased because of the somewhat faster degradation of the S-enantiomer (see below).

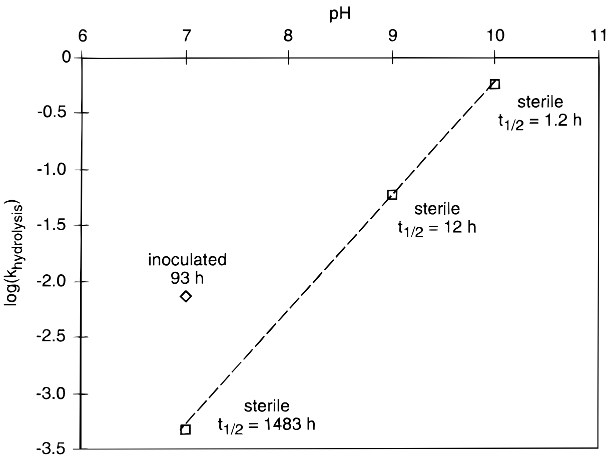

FIGURE 3. Initial hydrolysis reaction rates ($k_{hydrolysis}$) and half-lives ($t_{1/2}$) of Preventol B 2 in aqueous solutions at different pH and 25 °C. Numbers of samples and numbers of replicates per sample were as follows: pH 7, sterile, 3, 2; pH 7, inoculated, 2, 3; pH 9, sterile, 1, 1 and 3, 3; pH 10, sterile, 3, 3.

TABLE 1. Elution Rate of (*R,S*)-Mecoprop (M), Preventol B 2 (M-PEG-M), and/or the Intermediate Ester Alcohol (M-PEG) from a Selected Bituminous Membrane (Product 1)

conditions	total (*R,S*)-mecoprop[a] (μg m^{-2} h^{-1})	"free" (*R,S*)-mecoprop (μg m^{-2} h^{-1})
pH 7 (25 °C, sterile)	280	95 (45, 270)[b]
pH 7 (4 °C, sterile)	nd	18
pH 10 (25 °C, sterile)	640	nd
pH 10 (4 °C, sterile)	120	nd
pH 7 (25 °C, nonsterile)	680	360

[a] As (*R,S*)-mecoprop equivalents, sum of M, M-PEG, and M-PEG-M.
[b] Other membranes, products 2 and 3.

From the results of the restricted number of elution experiments that are summarized in Table 1, some qualitative conclusions can be drawn. First, when considering only the appearance of free (*R,S*)-mecoprop in solution, at pH 7 and 25 °C under sterile conditions, the elution rate varied by up to a factor of 6 between the three selected membranes from the three main producers in Switzerland. Furthermore, in contrast to the hydrolysis experiments (see above), the effect of pH and of the presence of microorganisms on the total amount of (*R,S*)-mecoprop (Preventol B 2 (M-PEG-M), the intermediate ester alcohol (M-PEG), and (*R,S*)-mecoprop (M)) eluted from a given membrane was found to be rather marginal (less than a factor of 3). Hence, diffusion of M-PEG-M, and possibly of M-PEG out of the membranes appears to be a rate-limiting process that is not significantly affected by pH and, particularly, by microbial activity. On the roofs, however, other biological factors such as penetration of roots into the membranes may enhance the leaching process. Furthermore, microbial processes may strongly influence the actual concentration of "free" (*R,S*)-mecoprop in the aqueous phase on the roof in two ways. On the one

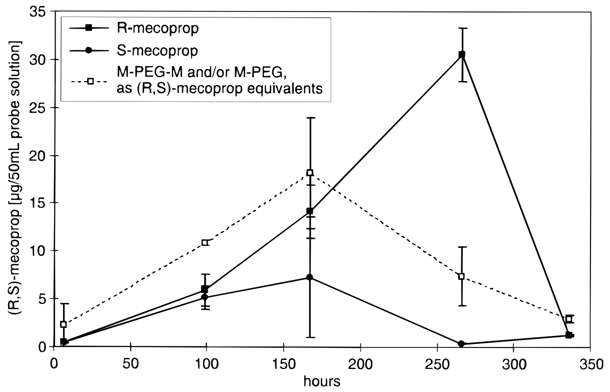

FIGURE 4. Elution of *R*-mecoprop, *S*-mecoprop, Preventol B 2 (M-PEG-M) and/or M-PEG [given as (*R*,*S*)-mecoprop equivalents] from a selected bituminous membrane (Product 1) at pH 7 and 25 °C with inoculum.

TABLE 2. (*R*,*S*)-Mecoprop Concentrations in Overlaying Water or Runoff from Different Roofs

roof	date/location	*R*-mecoprop (µg/L)	*S*-mecoprop (µg/L)	(*R*,*S*)-mecoprop (µg/L)
1	summer 96/Zurich[a]	1.4	2.2	3.6
2	summer 96/Zurich[a]	1.6	1.7	3.3
3	summer 96/Zurich[a,c]	<0.03	<0.03	<0.03
4	June 97/Grüze[b,d]			3.3
4	November 97/Grüze[b,e]			1.5
4	August 97/Grüze[b,f]			~500[g]

[a] Overlaying water. [b] Roof runoff. [c] Membrane without Preventol B 2. [d] Average concentrations of 30 samples, 5 days, average temperature 13.4 ± 2.4 °C. [e] Average concentrations of 19 samples, 4 days, average temperature 3.4 ± 1.7 °C. [f] Single sample: 18 days of dry period with average temperature 21.2 ± 4.8 °C before sampling. [g] Not quantifiable with the trace analytical method applied.

hand, as discussed above, the microbially catalyzed hydrolysis of M-PEG-M and M-PEG is much faster at ambient pH as compared to the abiotic process. On the other hand, as is illustrated by Figure 4, both *R*- and *S*-mecoprop were biodegraded. In this case, the S-eantiomer was more easily degraded than the R-enantiomer which is consistent with the results of other studies (*7, 8*), and which may be of crucial influence for the ER established at a given time. Finally, it should be noted that the ER may also be affected by microbially catalyzed racemization (*7*).

In summary, the results of these preliminary model experiments demonstrate that the amount of (*R*,*S*)-mecoprop released into roof runoff from a given flat roof is significant but depends on various processes that are quite difficult to quantify. Hence, field data determined under natural conditions are necessary to estimate the order of magnitude of release of this compound from flat roofs into the environment.

Field Studies. The (*R*,*S*)-mecoprop concentrations determined in water samples taken from either the surface or the runoff of different roofs equipped with Preventol B 2 containing bituminous sheets are summarized in Table 2. The concentrations varied from 1.5 to 4 µg/L, except the very high concentrations measured after an 18 day dry period with an average temperature of 21.2 ± 4.8 °C in August 1997 (ca. 500 µg/L). The lower concentrations during the winter months may be rationalized with both the reduced hydrolysis rate (see Table 1) and the diminished microbial activity at lower temperatures. Note that, in contrast to the findings from laboratory experiments, where Preventol B 2 was found to be directly eluted from bituminous membranes, no Preventol B 2 or M-PEG was found in roof runoff of roof 4 (Table 2). Presumably, the root-protecting agent is retarded in the overlaying roof layers or soil material, where subsequent hydrolysis may take place.

A more detailed study over a period of 5 days was conducted at the field site Grüze, where the combined roof runoff of three roofs with a total area of about 5100 m^2 is infiltrated into the subsurface (for details, see ref *1*). The two main flat roofs (3860 and 715 m^2, respectively) were both equipped with identical Preventol B 2 containing sealing membranes. The larger one was covered with gravel, whereas the other one had an intensive greentop planting on the surface. These two roofs are comparable to the earlier discussed model roofs. The third roof was a fast discharging polyester roof of 485 m^2 and was not a source of (*R*,*S*)-mecoprop but diluted the combined runoff with rainwater. Rainwater, collected over the sampling period, contained less than 35 ng/L (*R*,*S*)-mecoprop. Figure 5 shows, however, that (*R*,*S*)-mecoprop was continuously detected in roof runoff at much higher concentrations (up to 35 µg/L). The concentrations were heavily influenced by the actual flow, as well as by the foregoing weather situation. For example, the high rain intensity at the start caused a pronounced dilution of (*R*,*S*)-mecoprop at the onset of the runoff, where concentrations between 0.1 and 4.2 µg/L were measured. These first samples from 6/18/97, 00:00 until 05:30, exhibited a significantly enhanced (*R*,*S*)-mecoprop ER (1.36 ± 0.12), as compared to all the subsequent ones (0.99 ± 0.09). This indicates, as already observed in the laboratory experiments, that an enantioselective biological degradation of (*R*,*S*)-mecoprop occurred during the preceding 3 days with very little precipitation (1.5 mm, which was not enough to cause any roof runoff, but kept the roof sufficiently moist for hydrolysis and enantioselective degradation of the analyte). With decreasing flow, concentrations increased, reaching a maximum value up to 35 µg/L. In contrast, a moderate onset of roof runoff (Figure 5, events two and four) after a dry period flushes the (*R*,*S*)-mecoprop that had been produced since the last rain event. Hence, concentrations were elevated at the beginning of such events. Note that the (*R*,*S*)-mecoprop concentrations in the overlaying water sampled at the roof surface were generally considerably lower than the one in the roof runoff itself, which means, that the data in Table 2 for roof surface waters do not necessarily reflect the actual concentrations in the respective runoff, and that care must been taken when designing sample strategies for the assessment of (*R*,*S*)-mecoprop from such roofs. The average concentration in roof runoff over the period investigated was 3.3 µg/L, and the cumulative load of (*R*,*S*)-mecoprop over the 5 days under investigation was 630 mg (Figure 5). Assuming an annual rain amount of 1200 mm, of which around 80% passes the roof system of the investigated stormwater infiltration site, and an average concentration of 3.3 µg/L, an estimated annual load of 12 g is eluted from the roof system. An annual washout rate would then be 2.4 mg/m^2, or about 0.09‰ of the total Preventol B 2.

The large variability of (*R*,*S*)-mecoprop concentrations in different roof runoffs and at different times indicates the pivotal role of the type of roof, the type of rain event, and the history before the event. For further, more general considerations and mass flux calculations, however, the (*R*,*S*)-mecoprop concentration in roof runoff, its ER, and the annual washout rate from a roof can be assumed to be about 4 µg/L (range 1−500 µg/L), 0.8−1.4, and 0.1‰, respectively.

(*R*,*S*)-Mecoprop Loads from Roofs and from Agricultural Applications into the Environment. Roughly, about 300 t, and 30 t/year, of the root protection agent is currently present or used on flat roofs in Switzerland. At an average elution rate of about 0.1‰/year, a total of about 30 kg of (*R*,*S*)-mecoprop is eluted from flat roofs per year. Another estimation, assuming a rainfall of 1200 mm of which 70%

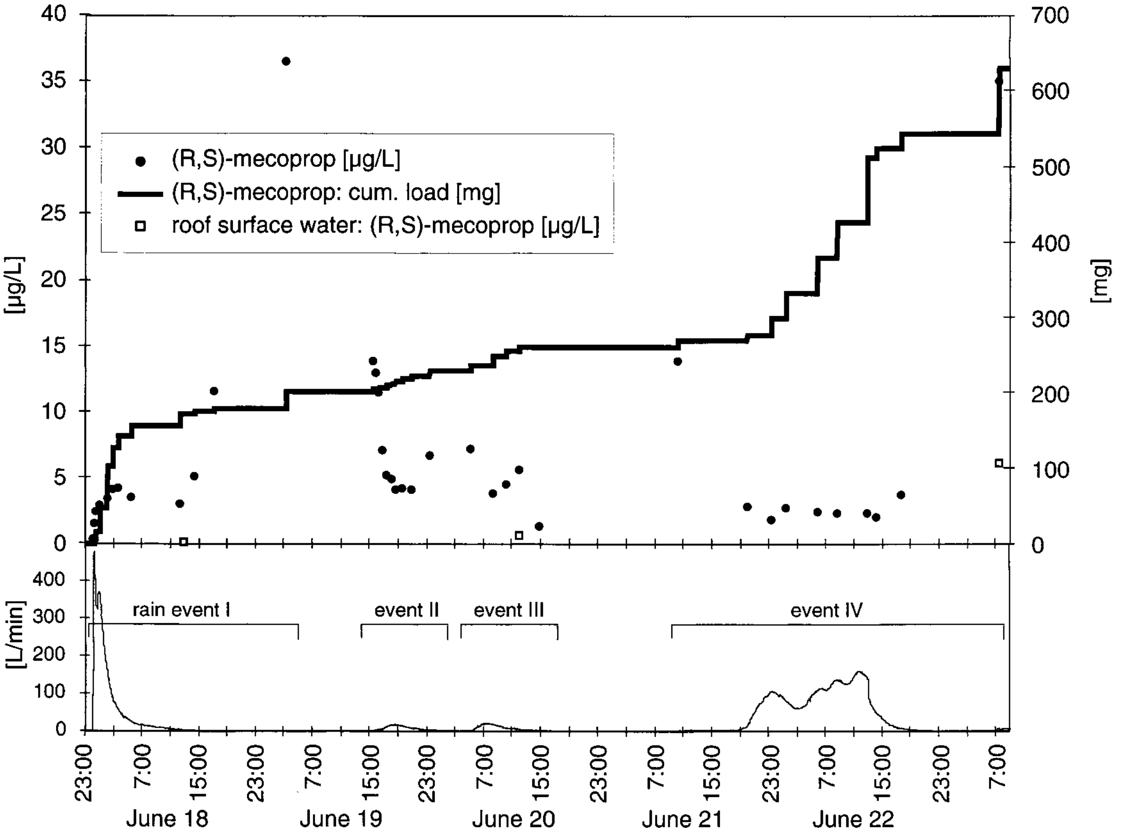

FIGURE 5. (*R,S*)-Mecoprop concentrations and cumulative load in roof runoff (upper box) and runoff flow rate (lower box) into the stormwater infiltration site in Grüze (June 17–23, 1997). The four rain events indicated in the lower box are referred to in the text. (*R,S*)-Mecoprop concentration in the corresponding rainwater was 35 ng/L.

leads to a runoff with an average (*R,S*)-mecoprop concentration of 4 μg/L (area 600 ha) leads to a very similar washout of about 20 kg. Presently, the discharge of roof runoff is mainly by combined sewer systems WWTPSs and therefore into surface waters (see Figure 6 a, and below). For comparison, the agricultural use of *R*-mecoprop in Switzerland is about 30 t/year, of which up to a few percent (for review see ref *9*) may reach the surface and/or groundwater (30–300 kg, assuming 1‰ to 1%, Figure 6c), and therefore, both sources might be equally important for these waters.

A Field Study in the Lake Greifensee Catchment Area. A field study in the Greifensee catchment area from October to December 1997, after the application period of mecoprop in agriculture, revealed that (*R,S*)-mecoprop concentrations in river waters were surprisingly high. With an average number of 106 ± 175 ng/L ($n = 17$), they were in the same concentration range as the still most widely used herbicide atrazine (69 ± 54 ng/L, $n = 17$). Detailed measurements in rivers, WWTPs effluents, and in the lake water revealed that a significant input of mecoprop into surface waters occurred through WWTPs. For example, the (*R,S*)-mecoprop load into the river Aabach increased by a factor 25 before and after the WWTP Gossau, the first WWTP of the rivers catchment area. Rough input calculations of (*R,S*)-mecoprop loads into the lake showed that the source of about 50% of the total measured (*R,S*)-mecoprop input were the nine WWTPs effluents in the catchment area (effluent concentrations up to 1.5 μg/L, ER about 0.65). This clearly shows the importance of WWTPs as sources of (*R,S*)-mecoprop. Since in Switzerland only *R*-mecoprop is allowed for agricultural applications, the ER of 0.65 in the WWTP effluent is a hint that a racemic source of (*R,S*)-mecoprop must be present (see ref *10*). These findings suggest that, for example, Preventol B 2 containing bituminous sealing membranes might be a major source of (*R,S*)-mecoprop in surface waters in highly populated areas.

Direct Infiltration of Roof Runoff. Another aspect to be considered in the future is the fact that, due to the propagation of direct infiltration of roof runoff into the subsurface, a substantial part of the current (*R,S*)-mecoprop load into WWTPs is prone to contaminate the groundwaters (see Figure 6b). Moreover, whereas a certain elimination of (*R,S*)-mecoprop may be assumed within the WWTPs, this is less likely to occur via direct discharge or infiltration of stormwater. Also, whereas the input by agricultural usage may be more diffuse, roof runoff infiltration may act as point sources. Hence, on a local scale, groundwater contamination due to infiltration of roof runoff may by far exceed the one caused by agricultural usage. These findings should be considered when designating contribution areas around drinking water wells or springs, as recommended by experts (*11*). Additionally, mecoprop is only registered as *R*-mecoprop as a herbicide, but the racemic mixture is used in the production of Preventol B 2. Thus, an unregistered herbicide/compound, namely *S*-mecoprop, is continuously introduced into the environment.

The presented findings suggest that the environmental benefits due to extended rooftop greening (*12*) should be newly assessed. Clearly, solutions other than the use of Preventol B 2 should be pursued to ensure the sealing of such roofs. Also, the use of Preventol B 2 violates the Swiss ordinance relating to environmentally hazardous substances that prohibits the application of pesticides on roofs. Conclusively, Preventol B 2 stands as a representative of widely used construction chemical biocides. Material protection agents other than Preventol B 2 ((*R,S*)-mecoprop) are used for example in architectural coatings, that is, Irgarol, which is known as an antifouling agent for boats, and diuron, a widely used herbicide. They may enter the environment through pathways unsuspected or unanticipated by produc-

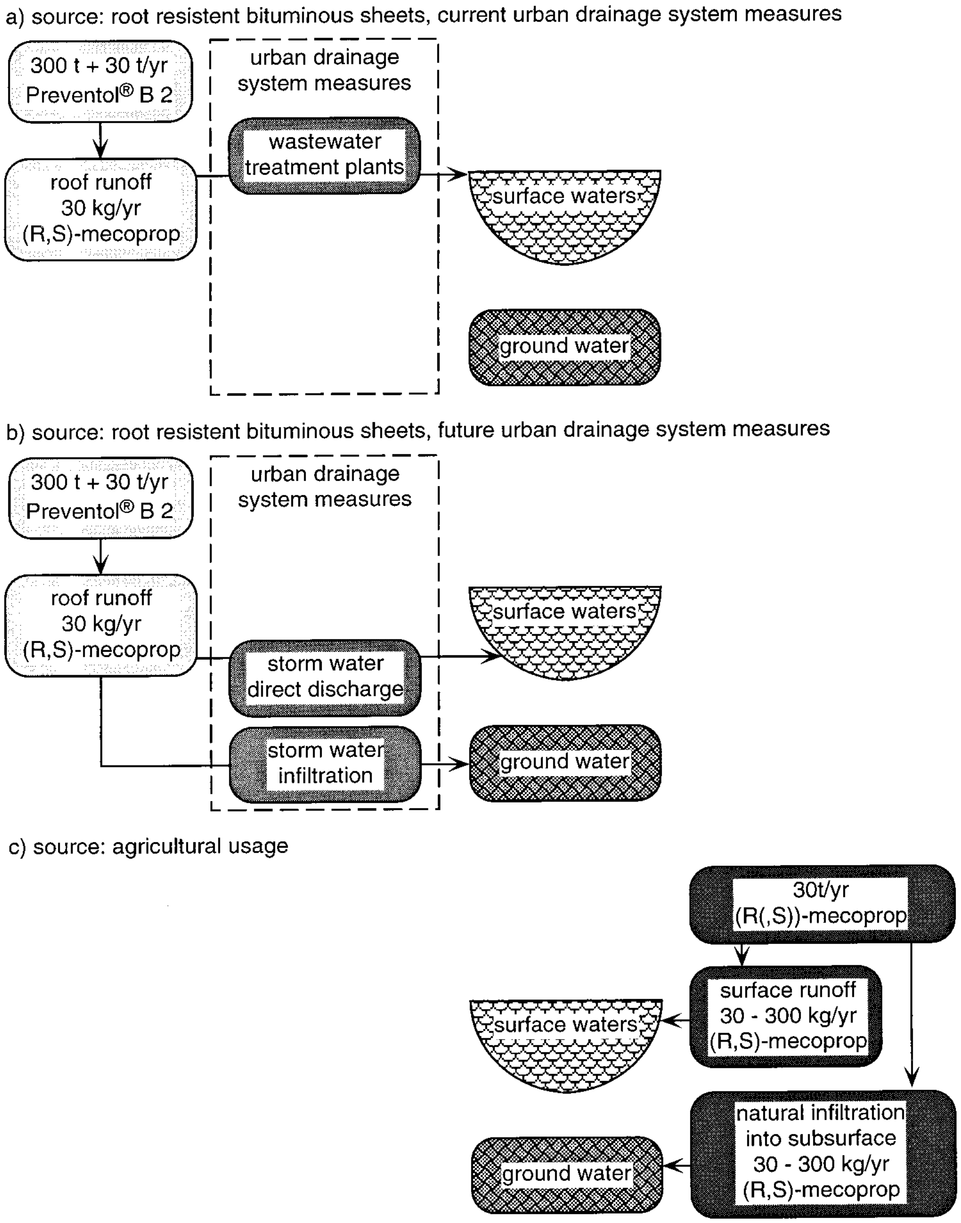

FIGURE 6. Annual (*R*,*S*)-mecoprop flow for different sources and urban drainage system measures. Note that the hitherto unknown input into the environment from bituminous membranes via roof runoff (a and b) is estimated to be in the same order of magnitude as the one caused by agricultural usage (c).

ers and consumers. These pathways are currently under investigation in our laboratory.

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